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MESA+
INSTITUTE FOR NANOTECHNOLOGY

Candidate: Swaraj Rashmi Pradhan
Thesis title: 'Nanoengineering of Thin Layers Of Semiconductor Photocatalysts In A Microreactor Environment For Lignin- Based Model Compounds Valorization'

Reviewer's Report

This thesis is concerned with a novel chemical engineering approach to synthesize thin layers of materials. To assist in this objective, the candidate has used ultrasound techniques and tuning catalytic properties of tubular reactors. The chosen modification approach to functionalize the inner walls of the reactor was using fluoropolymer to ensure the selective oxidation of lignin-based model compounds.

The choice of topic is a brave one. Attempts to make something useful out of lignin are abundant, with varied level of success. In choosing ultrasound and microfluidics, I believe there is evidence of a good understanding of where the field has evolved. Continuous flow reactors that take advantage of the 'green' character of ultrasound (as an advanced oxidation process technology) have been demonstrated and the scientific community is focusing for good reasons on them.

The thesis is clearly structured in five chapters. The research hypotheses (four in total) are connected to two corresponding objectives and an introduction to the topic (Chapter 1). Chapter 2 is a comprehensive state-of-the-art review on microflow reactors and ultrasound approaches, followed by a compilation of methods for TiO2 immobilization at the surface (inner walls) of the microreactor.

In Chapter 3 the candidate explains how a thin layer microreactor system is used for selective photocatalytic partial oxidation of benzyl alcohol as a lignin-based model compound. This I consider it to be the proof-of-concept of this thesis. A) Using a microreactor system which shows better photo-reactivity of test/reaction-molecules: benzyl alcohol conversion and benzyl aldehyde selectivity. B) Investigating if ultrasonication (US) assists in the coating process and mass deposition enhancement, that can improve photoreactivity compared to the silent (no ultrasound) alternative.

The following Chapters are a step further in optimizing and characterizing the coating. In Chapter 4 we see how a pre-developed sol-gel method can be used to synthesize monometallic TiO2, and we learn about which atomic percentage of metal on TiO2 and characterized corresponds to specific photocatalytic activity. Chapter 5 explains how a bimetallic TiO2 catalyst can improve the photocatalytic activity under visible light.

Points that could be clarified during the PhD defense or improved in the text if possible or desired by the tutor:

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- In Figure 4, chapter 2, the candidate shows the number of publications reporting a combination of ultrasound and microfluidics. At first sight this could be seen as a modest number, but it is important to remember that industry tends to keep competitive information secret. Where else could we find information that points at the relevance and future prospects of this technology?
- If we agree that ultrasound and microreactor technology can lead to greener alternatives, what can be said about the materials used for the reactor themselves? Also, what type of electricity can be used to power the ultrasonic equipment, coming from what type of energy source?
- I missed some discussion about the effect of ultrasonic parameters, e.g., frequency and pressure amplitude. Only in some parts, e.g., p57, 69, 81, Appendices, we find that 37 and 80 kHz were used, but no reasoning behind it is given.
- I would like the candidate to clarify the relation between the topic of the section and some of the referenced work. For example, in p.47 "These types of reactors are broadly used in laboratories and industrial applications, but the analysis and comparison of results obtained with them are extremely difficult, which has limited the scaling-up of sonochemical reactors in the industry" citing Chem. Eng. Process. Process Intensif., 2018, 123, 221–232.
- I found references (mostly in the introductory parts of the thesis) regarding the probability of observing clogging in the reactor channels. Was there any clogging during the experimental work? If not observed, why is that the case, and how was it avoided?
- I would expect some discussion on the adhesion of the catalyst to the walls of the reactor. How was that measured? In this line, for how long is the surface of the catalyst active? – Does it need reactivation or some sort of process to extend lifetime/operation?
- Could the candidate discuss if there is an advantage to be found in using novel ways to monitor and control reactions in microreactors, e.g., machine learning or artificial intelligence? As a way of finding optimized conditions perhaps?
- The text in several Figure's captions could have been better presented and more explanatory.

Despite my list of points of improvement, considering the relevance of engineering work and challenge integrating the knowledge, tools and concepts, I am of the opinion that the doctoral dissertation meets the conditions specified in Article 187 of the Act of July 20, 2018 Law on Higher Education and Science (Journal of Laws of 2022, item 574, as amended).

I also believe that the reviewed work deserves distinction, and hereby I provide the most salient arguments behind my proposition:

- Five peer-reviewed publications and one patent application before finalizing the Thesis is not common. I see it as a sign of arduous work and the ability of the candidate to collaborate with the supervisor and collaborators (listed as co-authors). This is a

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proxy of maturity of the candidate as a scientist, and the potential of becoming a leading researcher in the future.

- Bridging the activities of material synthesis, characterization and application in a mircroreactor is not easy feat. From Materials Science, Chemistry and Chemical Engineering, this thesis demonstrates a seamless transition from the smallest aspects, at the molecular level, up to the benchtop experimental details.
- The importance of the results presented in the thesis and potential of utilisation by industry will help advance the Advanced Oxidation Process (AOP) field. Ultrasound as a 'green' alternative to traditional synthesis and chemical transformations is in high demand.

Signed: David Fernandez Rivas

Date: 24.09.2023